

Sr₂(Ba₂)VO₄ under pressure – an orbital switch and potential d^1 superconductor

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We study Sr₂(Ba₂)VO₄ under high pressure by means of the local density approximation + dynamical mean field theory method. While Sr₂VO₄ is a 1/6-filling three-band system at ambient pressure with a small level splitting between the d_{xy} - and $d_{yz/zx}$ -bands, we show that an orbital polarization occurs under uniaxial pressure, resulting in dramatic changes of the magnetic, optical, and transport properties. When pressure is applied in the c -direction, a d^1 analog of d^9 cuprates is realized, making Sr₂(Ba₂)VO₄ a possible candidate for a d^1 superconductor. Experimentally, this uniaxial pressure can be realized by growing Ba₂VO₄ on a substrate with lattice constant 4.1-4.2 Å.

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Since the discovery of high temperature superconductivity in cuprates[1], strongly correlated electron systems (SCES) and their intriguing magnetic, dielectric, optical and transport properties have been at the center of solid state research. Hence, a quantitative reliable calculation of correlation effects from first-principles is one of the most important challenges. This is particular difficult since the standard local density approximation (LDA) in the framework of density functional theory[2] fails if electronic correlations are strong. Recently however, a variety of attempts which go beyond LDA have been undertaken, and many successes have been achieved[3].

The next step in this direction is the (theoretical) materials design of SCES with specific properties and the simulations of SCES under extreme conditions. As a touchstone for such attempts, we study the electronic structure of Sr₂VO₄ and Ba₂VO₄ under high pressure by means of the LDA+DMFT (dynamical mean field theory) method[4], one of the most widely used approaches for realistic calculations of SCES [5].

The reason why we focus on Sr₂VO₄ is twofold. First, Sr₂VO₄ is a layered perovskite, as cuprates and ruthenates[6] which show unconventional superconductivity. Second, the challenge to synthesize single-crystalline Sr₂VO₄ has been overcome quite recently: One of the authors and his coworkers[7] employed epitaxial growth techniques for growing a thin Sr₂VO₄ film. Hence, a detailed investigation of the electronic structure becomes now possible.

As for the first point, in fact, Sr₂VO₄ attracted attention because it is a "dual" material of La₂CuO₄. Namely, the former has one 3d electron per V site (d^1 system), while the latter has nine 3d electrons per Cu site (d^9 system). However, as was already pointed out by Pickett *et al.* in 1989[8], there is a big difference between these oxides. While La₂CuO₄ is a 1/2-filling single-band ($d_{x^2-y^2}$) system, Sr₂VO₄ is a 1/6-filling three-band ($d_{xy}/yz/zx$) system, since the level splitting of t_{2g} in the latter mate-

rial is much smaller than that of e_g in the former. Therefore, the theoretical idea of unconventional superconductivity in Sr₂VO₄ has been dismissed.

Also experimentally, Sr₂VO₄ and La₂CuO₄ behave indeed differently. Magnetic properties and transport properties were measured for a polycrystal of Sr₂VO₄ in the early 1990's[9], indicating that Sr₂VO₄ is an antiferromagnetic insulator (semiconductor) with a low Néel temperature $T_N \sim 45$ K. But in contrast to La₂CuO₄, a small ferromagnetic moment was also observed. In recent measurement of the optical conductivity for a single-crystalline thin film, a small gap structure, i.e., a peak around 1 eV and a shoulder around 0.5 eV was observed[7].

Theoretically, several first-principles calculations beyond LDA were performed, and it was confirmed that the relation between Sr₂VO₄ and La₂CuO₄ is not dual[10, 11]. Especially, Imai *et al.* carried out an LDA+PIRG (path integral renormalization group) calculation and found a nontrivial orbital-stripe order[10]. These orbital degrees of freedom are irrelevant in cuprates.

The motivation of the present study is based on the following idea: While Sr₂VO₄ and La₂CuO₄ are certainly not dual at ambient pressure, we hope to change this by changing the atomic configuration of the octahedron around the V ion. Here we consider to apply high uniaxial pressure, synthesize films on substrates with appropriate lattice constant, and introduce chemical pressure (substitute Sr by Ba). If the level splitting between the d_{xy} and $d_{yz/zx}$ orbitals becomes larger, it will lead to an orbital polarization, so that the system might actually become a d^1 analog of d^9 cuprates. In this Letter, we examine this idea by means of LDA+DMFT.

GGA optimization of crystal structure. Let us now turn to our actual calculations. First, we perform a GGA (generalized gradient approximation) calculation with plane-wave basis, employing the Tokyo Ab-initio Program Package (TAPP)[12]. Note that a plane-wave

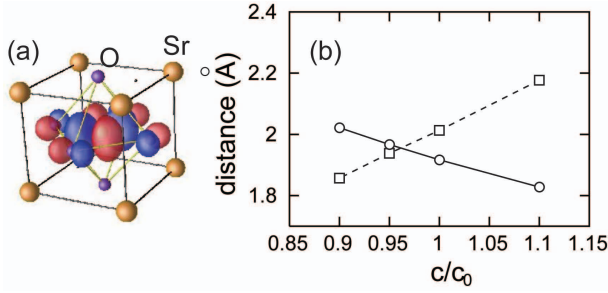


FIG. 1: (a) Atomic configuration of Sr_2VO_4 together with the NMTO Wannier function of the V d_{xy} -orbital. The position of Sr and the apical oxygen are optimized by a plane-wave GGA calculation. (b) GGA-optimized distance between O and V along the c direction (open squares) and in the ab -plane (open circles) as a function of the c axis elongation c/c_0 .

basis set has advantages for optimizing atomic configurations under high pressure which are unknown experimentally. We adopt the exchange-correlation functional introduced by Perdew *et al.*[13] and ultra-soft pseudopotentials in a separable form[14, 15]. The wave functions are expanded up to a cut-off energy of 36.0 Ry, and $8 \times 8 \times 8$ and $12 \times 12 \times 12$ k -point grids are used. We assume that the system has the same $I4/mmm$ symmetry as at atmospheric pressure [16], so that there are only two free parameters, i.e., the position of the apical oxygen and Sr. In Fig. 1(a), we show the atomic configuration of the octahedron around the V ion.

We calculate the total energy as a function of the lattice constant a , fixing the ratio c/a to its experimental value ($=3.28$)[9]. We find that the energy minimum is at $a=3.89\text{\AA}$ (not shown), in excellent agreement with experiment ($a=3.84\text{\AA}$). When the lattice constant a is fixed to this optimized value, the Sr-V and O-V distances along the c -direction become 4.46\AA and 2.01\AA , respectively, consistent with the experimental values 4.46\AA and 1.98\AA .

Next, we change the lattice constants to simulate the effect of pressure. Considering to apply high uniaxial pressure or, more realistically, to synthesize Sr_2VO_4 films on substrates with appropriate lattice constant, we change the lattice constant c up to $\pm 10\%$ of the experimental value $c_0 = 12.76\text{\AA}$.

In Fig. 1(b), we plot the GGA-optimized distance between O and V along the c -direction (d_c) and within the ab -plane (d_{ab}) as a function of c/c_0 . Here we fix the volume of the unit cell (V) rather than a , since the total energy at fixed V is always lower than that of fixed a . While the V-O distance d_c is longer than d_{ab} at ambient pressure, d_c becomes shorter than d_{ab} for $c/c_0 < 0.95$.

In fact, the ratio d_c/d_{ab} determines the splitting of the three t_{2g} orbitals. If we press uniaxially along the c -direction, the negatively charged oxygen ions move towards the vanadium site. Hence the energy of the $d_{yz/zx}$ -orbitals, which point along the c -direction, is enhanced. At ambient pressure the level splitting is small. But given

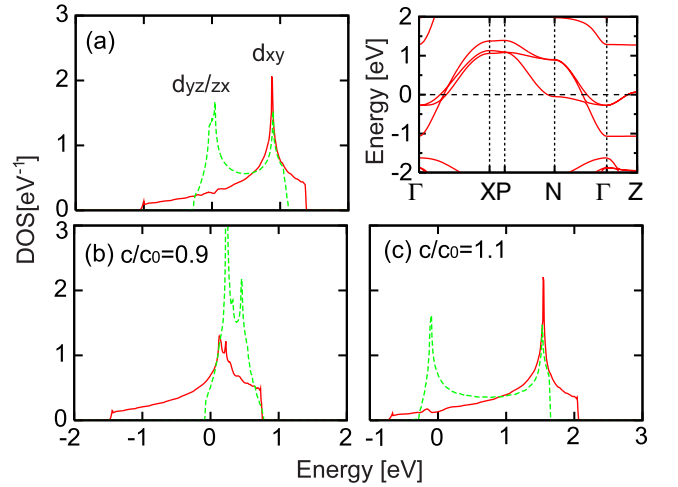


FIG. 2: Density of states of the t_{2g} band for (a) atmospheric-pressure, (b) uniaxial pressure in the c direction ($c/c_0 = 0.9$), and (c) uniaxial pressure in the ab plane ($c/c_0 = 1.1$). Solid (dashed) line is for the d_{xy} -orbital ($d_{yz/zx}$ -orbitals). Inset: LMTO band structure for atmospheric-pressure.

the fact that d_c and d_{ab} change considerably with c/c_0 in Fig. 1(b), we may expect that we can control the level splitting, and, consequently, the orbital occupation by applying pressure.

LDA+DMFT calculation. To examine this idea in the presence of electron correlations, we perform LDA+DMFT calculations for the atomic configurations obtained above. To this end, we first carry out LDA band structure calculations with the LMTO (linearized muffin tin orbital) basis[17]. In the inset of Fig. 2, we show the obtained band structure for ambient pressure. Almost the same band structure is obtained by the GGA calculation with plane-wave basis.

Then, we extract the three t_{2g} bands by the NMTO (N -th order muffin tin orbital) downfolding[18], using the generated LDA potential. As a typical example of the resulting NMTO Wannier functions, we show the d_{xy} -orbital of V in Fig. 1(a) for ambient pressure. The density of states (DOS) of the t_{2g} band for $c/c_0 = 0.9, 1.0$ and 1.1 are shown in Fig. 2. The NMTO band width of the d_{xy} -band is 2.46 eV at ambient pressure ($c = c_0$). This value is consistent with that of the GGA calculation with plane-wave basis and that of Pickett *et al.* who used the full-potential linearized augmented plane wave (LAPW) basis[8]. Imai *et al.*[10] reported a smaller band width of ~ 2.0 eV[19].

For the case of $c/c_0=0.9(1.1)$, Fig. 2 shows that the center of gravity of the $d_{yz/zx}$ -bands is clearly higher(lower) than that of the d_{xy} -band. Indeed, the crystal field splitting between the d_{xy} - and $d_{xz/yz}$ -orbitals in the NMTO Hamiltonian is $-382(+434)$ meV for $c/c_0=0.9(1.1)$. Concerning the electron occupation of the d_{xy} - and $d_{xz/yz}$ -orbitals, 90%(20%) of the d electrons

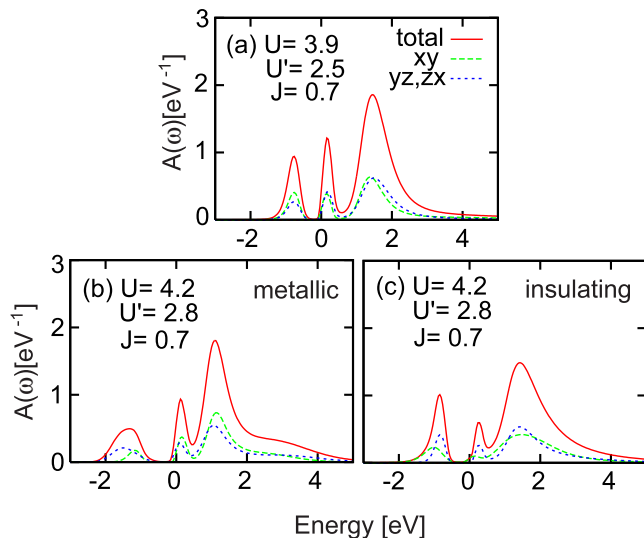


FIG. 3: LDA+DMFT spectral function for atmospheric-pressure, where dashed, dotted, and solid line are for d_{xy} , $d_{xz/yz}$, and the total Sr_2VO_4 spectrum, respectively. For $U' = 2.8$, two solutions [metallic (b) and insulating (c)] co-exist.

are accommodated in the d_{xy} -band for $c/c_0=0.9(1.1)$, in contrast to ambient pressure where all three t_{2g} bands are similarly occupied.

Next, we perform DMFT calculations for the three low-energy t_{2g} bands, studying whether electronic correlations result in a full orbital polarization for $c/c_0=0.9$ and 1.1 . To this end, the DMFT effective impurity model is solved by the standard Hirsch-Fye quantum Monte Carlo (QMC) method[20], where the temperature is 0.1 eV with 100 imaginary time slices and the number of QMC sample is $\sim 2 \times 10^6$. We employ the relation $U = U' + 2J$ where U , U' , J are the intra-orbital Coulomb interaction, the inter-orbital Coulomb interaction and the Hund coupling, respectively.

We first calculate the spectral function for ambient pressure with various interaction parameters U' , fixing $J=0.7$ eV which is a reasonable value for V ions. In Fig. 3, we show the spectral function for $U'=2.5$ eV (a) and 2.8 eV (b,c); the Mott-Hubbard transition occurs around $U'=2.5 \sim 2.8$ eV. Since the gap in (c) is in accord with the main optical peak in experiment[7], we expect $U' \sim 2.8$ eV for Sr_2VO_4 . The coexistence of this insulating solution (c) with a metallic one (b) indicates insulating Sr_2VO_4 to be close to a Mott-Hubbard transition.

Note that Imai *et al.* [10] estimated smaller Coulomb interactions: $U' \sim 1.3$ and $J \sim 0.65$ eV by the combination of the constrained LDA and the GW method[10]. However, as mentioned above, the band width of the t_{2g} -orbitals of Ref. [10] is 20-25% smaller than that of the present study. If we normalize the interaction parameters by the band width, the difference is not so big. On the other hand, Sekiyama *et al.* employed $U'=3.55$ and

$J=1.0$ eV in their LDA+DMFT calculation for SrVO_3 , reproducing the photoemission spectrum of SrVO_3 [21]. These values are not so far from ours.

Let us now turn to the LDA+DMFT results for high pressure. In Fig. 4(a), we plot the spectral function for $c/c_0 = 1.1$, showing a metallic peak at the Fermi level. In contrast to ambient pressure, there is no coexisting insulating solution at $c/c_0 = 1.1$, i.e., applying pressure in the ab plane makes Sr_2VO_4 metallic. An important point is that the d_{xy} -orbital is almost empty for $c/c_0 = 1.1$: orbital polarization occurs. The system becomes a quarter-filled 2-band Hubbard model which is well known to have a ferromagnetic ground state[22, 23]. Therefore, we expect ferromagnetic spin fluctuation to be dominant at low T if pressure is applied in the ab plane.

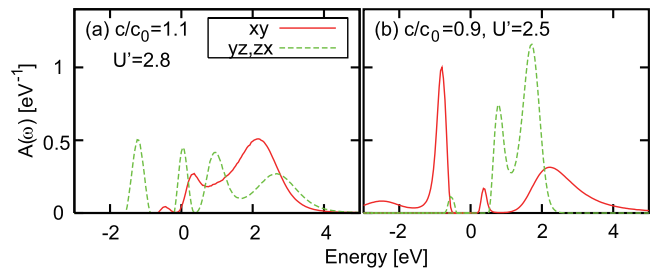


FIG. 4: Same as Fig. 3 but for (a) uniaxial pressure in the ab plane ($c/c_0=1.1$) with $U'=2.8$ and (b) uniaxial pressure in the c direction ($c/c_0=0.9$) with $U'=2.5$.

On the other hand, Fig. 4(b) shows the result for uniaxial pressure along the c direction ($c/c_0 = 0.9$). We see that the spectrum is now clearly insulating, even for the smaller value of $U' = 2.5$ for which we have a metal in Fig. 3(a). This is a surprising result: an inverse Mott-Hubbard transition. (Usually, applying pressure makes an insulator metallic, not a metal insulating as from Fig. 3(a) to Fig. 4(b).) What is the reason for this unusual behavior? From Fig. 2, we see that the LDA band width does not change strongly from 2.26 eV at $c/c_0 = 1$ to 2.46 eV at $c/c_0 = 0.9$. This small change of band width alone would indeed indicate more metallic behavior—as usual. But more important is that uniaxial pressure changes the crystal-field splitting: The two $d_{yz/zx}$ -orbitals become unoccupied, and then the large intra-orbital repulsion U makes the remaining (single) d_{xy} -orbital Mott-insulating. This way, a d^1 analog of d^9 cuprates is realized. Concerning the magnetic properties, we expect an antiferromagnetic instability since the system becomes a half-filled single-band model.

Ba_2VO_4 . While it is an interesting possibility to change the electronic properties by controlling the lattice constant, it might be difficult to change its value up to $\pm 10\%$. For example, in order to grow Sr_2VO_4 thin films with $c/c_0 = 0.9$, we need considerably large lattice mismatch between a substrate and bulk Sr_2VO_4 , while an excessive mismatch often results in lattice relaxation.

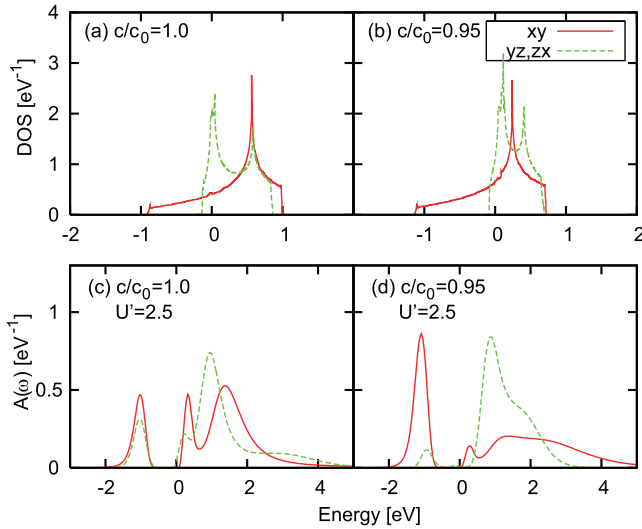


FIG. 5: Density of states of the t_{2g} band of Ba_2VO_4 for (a) atmospheric-pressure and (b) uniaxial pressure in the c direction ($c/c_0 = 0.95$). Figs. (c) and (d) are LDA+DMFT spectral function for (a) and (b) respectively, with $U' = 2.5$.

Thus, lastly, we consider the possibility of chemical pressure by substituting Sr by Ba. Since the ion radius of Ba is larger than that of Sr, the crystal is expected to be expanded. The important point here is that the V-O distance in the ab plane and that along the c axis will increase differently. Namely, while the increase of a directly affects the V-O distance in the ab plane (the latter is exactly half of the former), c and the V-O distance along the c axis are independent parameters.

First, we perform GGA calculation with structure optimization for Ba_2VO_4 by changing a and c . The energy minimum is at $a = 4.04$ Å and $c/a = 3.36$, the V-O distances are 2.02 Å in the ab plane (compared to 1.92 Å for Sr_2VO_4) and 2.01 Å along the c direction (2.01 Å for Sr_2VO_4). This means that the situation for Ba_2VO_4 is similar to that of Sr_2VO_4 with $c/c_0 = 0.95$, i.e., if uniaxial pressure is already applied.

Next, we consider the compression $c/c_0 = 0.95$ for Ba_2VO_4 . The orbital polarization becomes larger, i.e., the electron density is 0.73 for the d_{xy} band and 0.14 for the $d_{yz/zx}$ band. Thus it is interesting to proceed with DMFT calculations. In Fig. 5, we plot the resulting LDA+DMFT spectral function for ambient pressure and uniaxial pressure in the c direction ($c/c_0 = 0.95$) with $U' = 2.5$, along with the density of states by LDA. We can see that a large orbital polarization is realized even for $c/c_0 = 0.95$. Since the relative hopping and interaction parameters for the d_{xy} band are very similar to the cuprates, a d^1 analog of d^9 cuprates can be realized. Experimentally, the uniaxial pressure is best realized by growing Ba_2VO_4 on a substrate with a larger in-plane lattice constant 4.1-4.2 Å.

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